Energetic Ionic Liquids as TNT Replacements

T.W. Hawkins

Air Force Research Laboratory

Report Documentation Page

Form Approved
OMB No. 0704-0188

1. REPORT DATE **JUN 2005**	2. REPORT TYPE	3. DATES COVERED **-**
4. TITLE AND SUBTITLE **Energetic Ionic Liquids as TNT Replacements (Briefing Charts)**		5a. CONTRACT NUMBER 5b. GRANT NUMBER 5c. PROGRAM ELEMENT NUMBER
6. AUTHOR(S) **T Hawkins**		5d. PROJECT NUMBER **5026** 5e. TASK NUMBER **0541** 5f. WORK UNIT NUMBER
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) **Air Force Research Laboratory (AFMC),AFRL/PRSP,10 E. Saturn Blvd.,Edwards AFB,CA,93524-7680**		8. PERFORMING ORGANIZATION REPORT NUMBER
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)		10. SPONSOR/MONITOR'S ACRONYM(S) 11. SPONSOR/MONITOR'S REPORT NUMBER(S)
12. DISTRIBUTION/AVAILABILITY STATEMENT **Approved for public release; distribution unlimited**		
13. SUPPLEMENTARY NOTES		
14. ABSTRACT **N/A**		
15. SUBJECT TERMS		

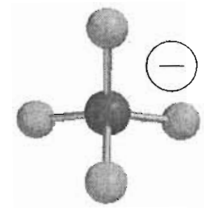
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT **unclassified**	b. ABSTRACT **unclassified**	c. THIS PAGE **unclassified**		**18**	

Standard Form 298 (Rev. 8-98)
Prescribed by ANSI Std Z39-18

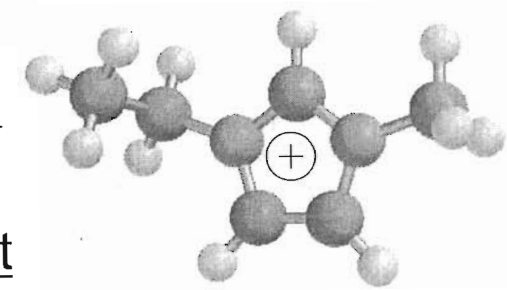
Energetic Ionic Liquids

- **Background**
  - An ionic compound that has a melting point at or below 100°C
  - Seminal work at USAFA
  - Industrial solvents, green chemistry
  - Ionic Liquids current focus area of AFOSR

  <u>AFRL now leading energetic IL discovery/development</u>



$AlCl_4^-$



EMIM cation

- **Advantages as Energetic Materials**
  - Low vapor pressure, low vapor toxicity
  - High density
  - Physical and chemical properties can be tailored

Can adjust these properties by:
- **Varying cation and anion**
  - **Size, shape, symmetry, composition, hydrogen bonding**
- **Creating mixtures, eutectics, etc.**

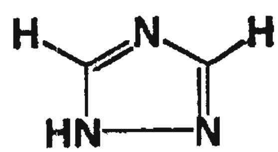
Ionic Liquids as TNT Replacements
– Objective –

- *ONR funded effort to identify and characterize ionic liquids suitable as a TNT replacement for melt-cast explosives*

Desirable Properties	Objective
Equivalent Explosive Performance (TNT)	Theor. Total Detonation Energy $\geq$ 7.7 (KJ/cc)
Castable	Melt Point Range of 70-100°C
Acceptable Small-Scale Hazards	Impact sensitivity > 200 Kg-cm Friction Sensitivity > 371 N
Thermally Stable	Pass Vacuum Thermal Stability Test (< 2cc gas/g @STP in 48 hrs at 100°C)
Simple Synthesis	Less than 3 Steps

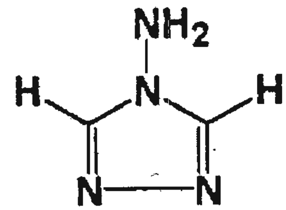
Precursors of Triazolium Salts for Evaluation

- High-nitrogen, heterocyclic precursors
- Relatively high formation enthalpy



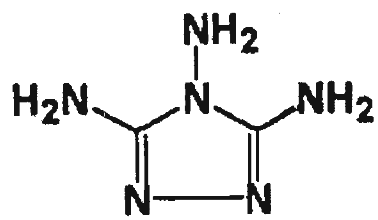
1-H-1,2,4-triazole
ΔH_f = +26 kcal/mol

"1,2,4-T"



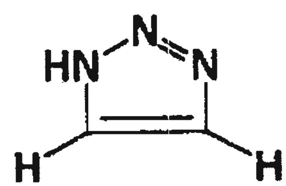
4-amino-1,2,4-triazole
ΔH_f = +50 kcal/mol

"4-AT"



3,4,5-triamino-1,2,4-triazole
ΔH_f = 0 kcal/mol

"TT"



1-H-1,2,3-triazole
ΔH_f (est)= +39 kcal/mol

"1,2,3-T"

Ionic Liquids as TNT Replacements

- **Good density and heats of formation obtained from nitrate and perchlorate salts**

Molecule	Density (g/cc)	Heat of Formation (kcal/mol)
TNT	1.65	-15*
1,2,4-T Nitrate	1.64	-34
1,2,4-T Perchlorate	1.85 (1.96**)	-17
4-AT Nitrate	1.62	-10
4-AT Perchlorate	1.82 (1.91**)	5
TT Nitrate	1.52 est.	-63
TT Perchlorate	1.72 est.	-48
1-Amino-3-Methyl-1,2,3 Triazolium Nitrate	1.63	20
1-Methyl-4-Amino-1,2,4 Triazolium Perchlorate	1.63	0

* Literature value

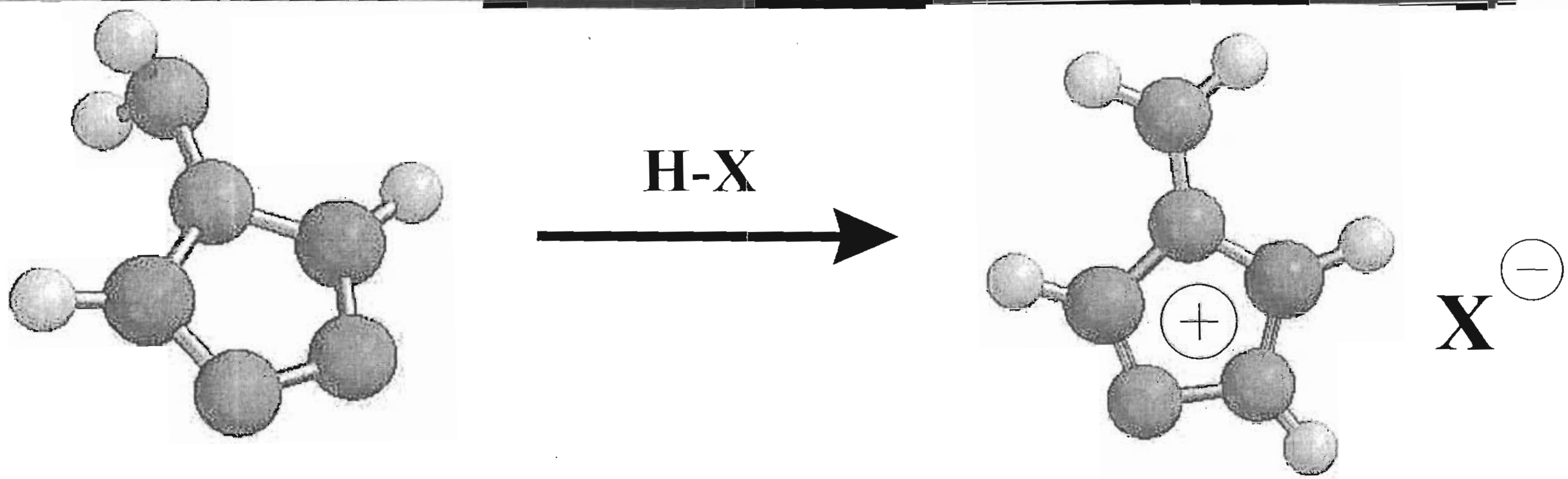
** X-ray crystallography

Properties of Synthesized Triazolium Salts

Molecule	Melt Point (°C)	Decomposition Onset (°C)	Thermal Stability @ 75°C (% wt. loss/day)	Impact Sensitivity* (kg-cm)
1,2,4-T Nitrate	137	182	0.88	>200
1,2,4-T Perchlorate	>250	285	0.02	114
1,2,4-T Dinitramide	75	120	0.29	98
4-AT Nitrate	70	180	0.58	>200
4-AT Perchlorate	83	242	0.02	30
4-AT Dinitramide	20	146	0.29	<5
TT Nitrate	206	245	0.20	>200
TT Perchlorate	194	275	<0.01	50
TT Dinitramide	145	160	0.13	196
1,2,3-T Nitrate	110	125	73.5	>200
1,2,3-T Perchlorate	73	200	0.05	<15
1,2,3-T Dinitramide	61	80	---	---
1-Amino-3-Methyl-1,2,3-T Nitrate	87	257	<0.01	>200
1-Methyl-4-Amino-1,2,4 Triazolium Perchlorate	85	245	<0.01	80

- Threshold initiation values where 5 consecutive "no go" results were obtained
- Drake, Hawkins, Brand, Hall, McKay, Vij and Ismail, "Energetic, Low-Melting Salts of Simple Heterocycles", *Propellants, Explosives, Pyrotechnics*, Vol 28, No. 4, 2003.
- Kaplan, Drake, Tollison, Hall and Hawkins, T., "Synthesis, Characterization, and Structural Investigations of 1-Amino-3-Substituted-1,2,3-Triazolium Salts,and a New Route to 1-Ssubstituted-1,2,3-Triazoles", *J. Heterocyclic Chem.*, Vol 42, No. 19, 2005.

Simple Heterocyclic Salts

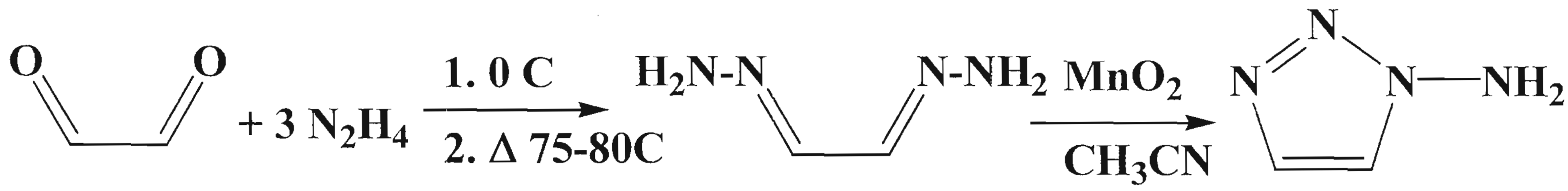


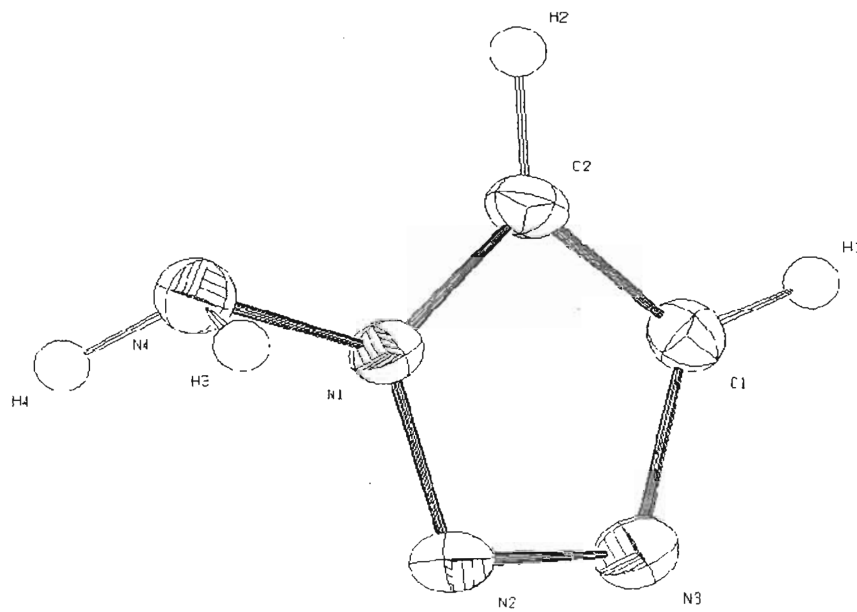
4-amino-1,2,4-triazole

SALT	Melting Point	Decomposition Onset
4-amino-1,2,4-triazolium nitrate	69° C	180° C
4-amino-1,2,4-triazolium perchlorate	84° C	242° C
4-amino-1,2,4-triazolium dinitramide	20° C	145° C

Ionic Liquids from 1-Amino-1,2,3-Triazole

Some ILs derived from effort with 1-amino-1,2,3-triazole

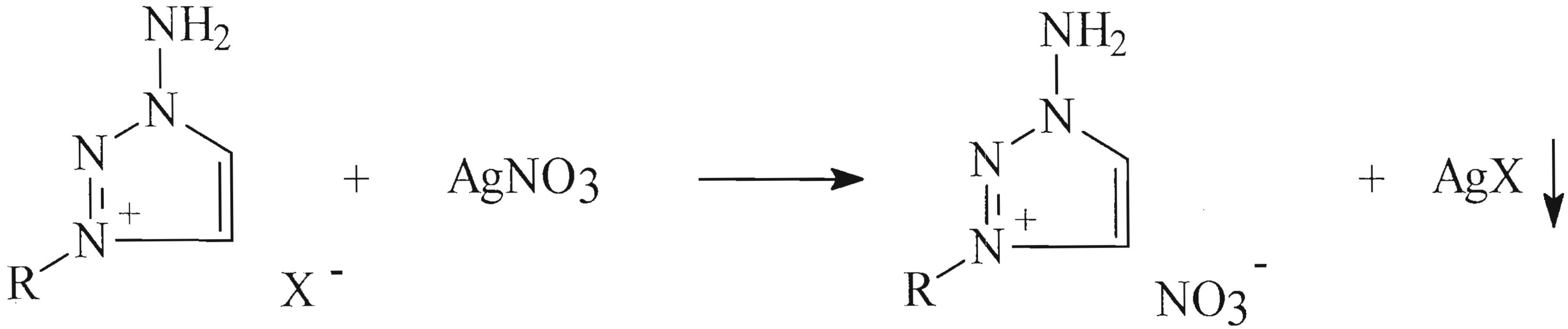




•Kaplan, Drake, Tollison, Hall and Hawkins, T., "Synthesis, Characterization, and Structural Investigations of 1-Amino-3-Substituted-1,2,3-Triazolium Salts,and a New Route to 1-Ssubstituted-1,2,3-Triazoles", *J. Heterocyclic Chem.*, Vol 42, No. 19, 2005.

AFRL Ionic Liquids

Metathesis forms desired nitrate salts



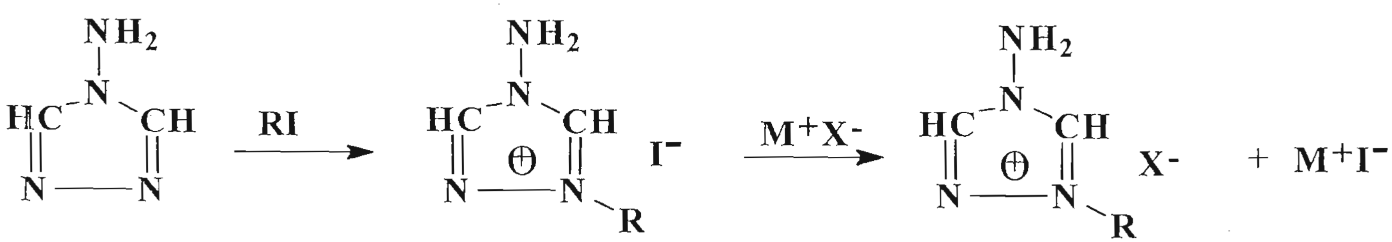
Ionic Liquids	M.P. (°C)
1-amino-3-methyl-1,2,3-triazolium nitrate (AMTN)	87
1-amino-3-ethyl-1,2,3-triazolium nitrate	30
1-amino-3-propyl-1,2,3-triazolium nitrate	33
1-amino-3-allyl-1,2,3-triazolium nitrate	8
1-amino-3-butyl-1,2,3-triazolium nitrate	48

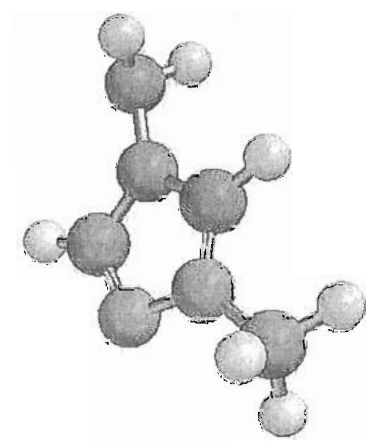
•Kaplan, Drake, Tollison, Hall and Hawkins, T., "Synthesis, Characterization, and Structural Investigations of 1-Amino-3-Substituted-1,2,3-Triazolium Salts,and a New Route to 1-Ssubstituted-1,2,3-Triazoles", *J. Heterocyclic Chem.*, Vol 42, No. 19, 2005.

Energetic Ionic Liquid Synthesis

Small-scale synthesis (10-g) of 1-methyl-4-amino-1,2,4-triazolium perchlorate

- Potential as TNT-replacement
- Not quite as energetic as the 1,2,3-triazole analog
  - But synthesis scheme requires half the number of steps (Scriven; Keay; Goe; Astleford J. Org. Chem. 1989, *54*, 731)
  - Synthesis is from commercial materials
  - High yield simple isolation
  - Simple halide salt metathesis to desired product
  - Usually over 90% yield for both steps
- Synthesis of bromide salt completed





1-methyl-4-amino-1,2,4-triazolium cation

"Distribution A: Public Release, Distribution unlimited."

Predicted Detonation Properties using Cheetah 4.0 Code*

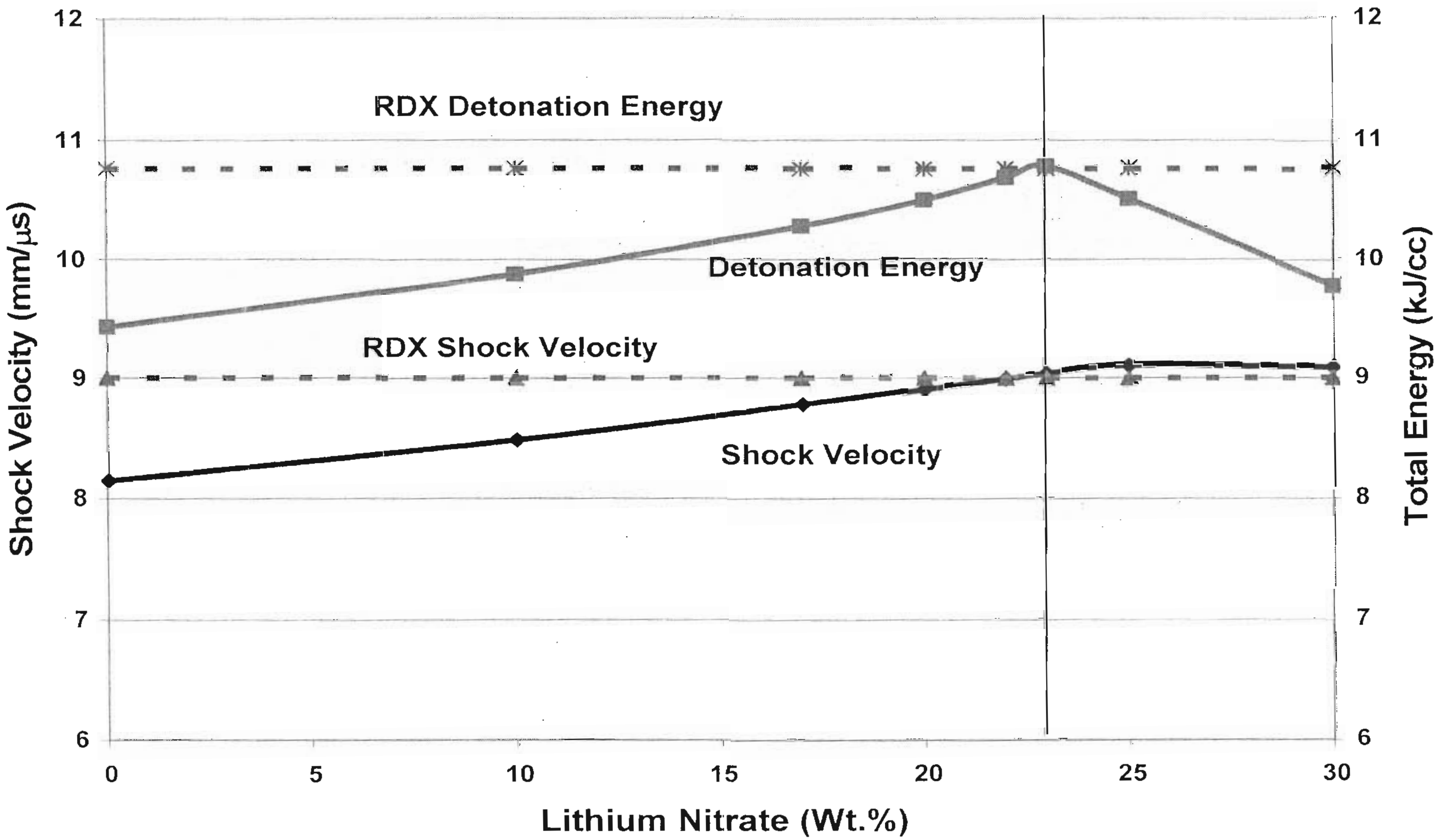
Calculations indicate that triazolium salts and mixtures are capable of achieving/exceeding performance goals

Ingredients (Composition, Wt/Wt)	Total Detonation Energy (KJ/cc)	Shock Velocity (mm/μs)	C-J Pressure (GPa)
TNT	7.389	6.843	17.90
4-ATP	8.911	8.516	31.39
1-AMTN	7.923	8.115	23.58
1-MATP	7.394	7.546	21.54

* Using new CHEETAH 4.0 Beta Version product library exp6.2

Ionic Liquid Mixtures (1)

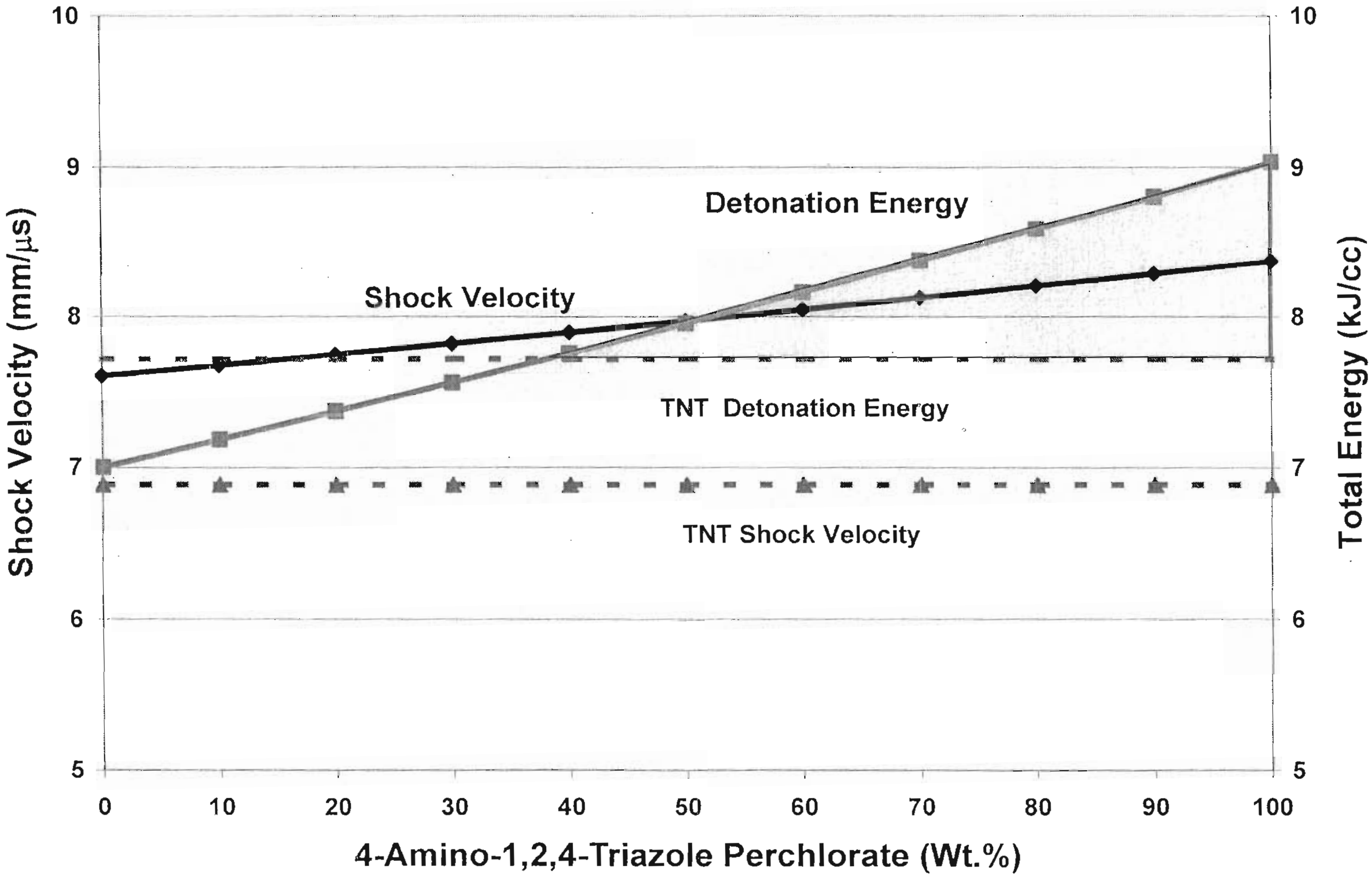
Theoretical Explosive Performance of Lithium Nitrate and 4-ATP



"Distribution A: Public Release, Distribution unlimited."

Ionic Liquid Mixtures (2)

Theoretical Explosive Performance of Mixtures of 4-ATN and 4-ATP



Predicted Detonation Properties using Cheetah 2.0 Code

Ingredients (Composition, Wt/Wt)	Total Detonation Energy (KJ/cc)	Shock Velocity (mm/μs)	C-J Pressure (GPa)
TNT	7.716	6.886	19.57
4-ATP	9.032	8.368	29.94
4-ATP/4-ATN (40/60)	7.756	7.895	24.49
4-ATP/TN (50/50)	7.720	7.915	25.10
4-ATP/TTN (76/24)	7.719	7.947	25.25
4-ATP/TTP (49/51)	7.728	8.027	26.15
TP	8.820	8.306	29.91
TP/4-ATN (45/55)	7.754	7.902	24.86
4-ATP/AN (47/53)	7.753	8.331	26.44
4-ATP/AP (66/34)	10.188	8.590	30.55
TP/AP (71/29)	10.045	8.505	30.23
RDX	10.444 (10.761*)	8.942 (9.000*)	34.74 (33.78*)
4-ATP/LiN (77/23)*	10.783	9.035	34.49
TP/LiN (80/20)*	10.481	8.786	33.70

* Optimized using the BKWS gaseous equation of state

Physical and Hazard Properties of Eutectic Mixtures

- Some eutectics could be identified with acceptable performance
- Tended to have relatively low melt points

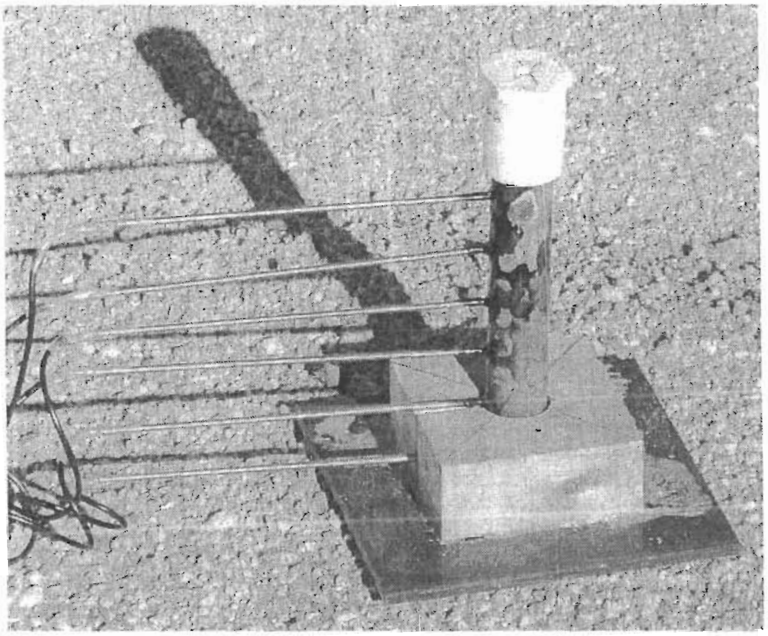
Ingredients (Composition, Wt/Wt)	Melt Temperature (°C)	Density at 25°C (g/cc)	Impact Sensitivity* (Kg-cm)	Friction Sensitivity* (N)
TNT	81	1.64	>200	>371
4-ATP	84	1.82	30	27
4-ATP/4-ATN (70/30)	63	1.63	138	88
4-ATP/4-ATN (30/70)	66	--	>200	>371
4-ATP/TP (70/30)	67	1.80	32	29
4-ATN	70	1.62**	>200	>371

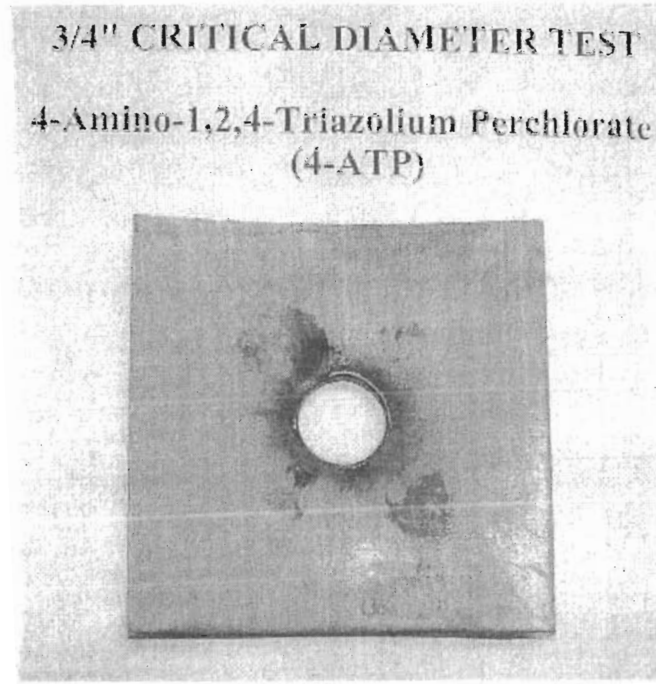
* Threshold initiation values where 5 consecutive "no go" results were obtained

** Density of the powdered material

Energetic Ionic Liquids for TNT replacements

Very promising initial results!!





Shock velocity determination

- 4-ATP (melt cast) ρ = 1.74 g/cm^3; shock velocity = 8.3 mm/usec
- TNT (pressed) ρ = 1.63 g/cm^3; shock velocity = 6.9 mm/usec (LLNL Data)

4-ATP is approaching energy output of high melt point nitramines like RDX

Ionic Liquids as TNT Replacements
Future Work

- Proposal for FY05 submitted (December 2004)
  - Synthesize MATP and AMTN for "rate stick" test
  - New energetic ILs identified as good theoretical performers
    - Pairing energetic triazolium cations with anions such as dinitrotriazolate and 5-nitraminotetrazole
- ONR-funded program
  - continues for FY05 (into FY06)

AFRL Ionic Liquids

Acknowledgements

Coworkers & Collaborators	Sponsors
Greg Drake (NASA-Marshall)	Judah Goldwasser (ONR)
Adam Brand (AFRL/PRSP)	Cliff Bedford (ONR
Milton McKay (AFRL/PRSP)	Mike Berman (AFOSR)
Stefan Schneider (AFRL/ERC)	Mike Huggins (AFRL/PRSP)
Les Hall (AFRL/PRSP)	Ronald Channell (AFRL/PRSP)
Mike Tinnirello (AFRL/PRSP)	Wayne Kalliomaa (AFRL/PRSP)
Donald Tzeng (AFRL/ERC)	Robert Corley (AFRL/PRS)
Leslie Hudgens (AFRL/ERC)	Ruth Doherty (NSWC-IH)